

Probing Ferroelectricity in Thin-film Perovskite SnTiO_3 with First-principles Structural Instability Analysis

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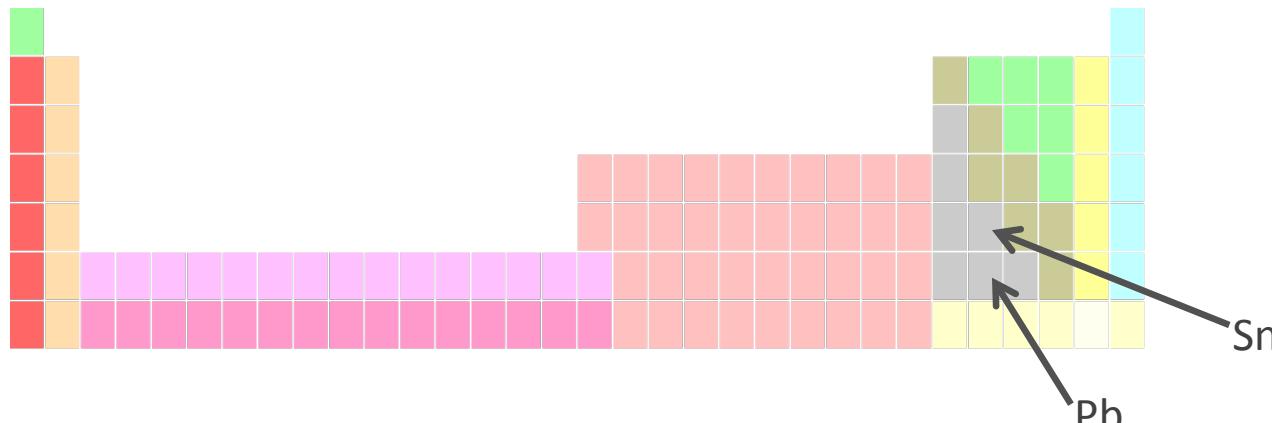
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Thin-film perovskite ferroelectric with tin has potential but may be challenging to make

- Tin is isoelectronic with lead and poses minimal health and environmental risks.



- Previous theoretical studies focused on bulk SnTiO_3 .
- Attempts to create bulk SnTiO_3 have failed (see Matar *et al.*, Chem. Phys. 2009). Can epitaxy help?
- One study suggests that non-polar $R\bar{3}$ (ilmenite) phase is more stable than polar $P4mm$ (Hautier *et al.*, Chem. Mat. 2010).
- Ultimately, we would also want to make a lead-free Goldstone ferroelectric (see Nakhmanson and Naumov, PRL 2010)



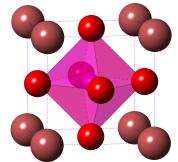
Computational methods used in this study

- Density-Functional Theory (DFT) plane-wave-based method to evaluate energies and compute/minimize forces on ions
 - ***Quantum ESPRESSO* package, <http://www.quantum-espresso.org/>**
- LDA with Vanderbilt ultrasoft pseudopotentials
- Unit cell parameters relaxed: stresses $\sigma_{\alpha\beta} = 0$.
 - Symmetry preserving algorithm by Wentzcovitch
- Density-Functional Perturbation Theory approach to compute Born effective charges and phonon bands in the Brillouin Zone
- Berry phase method and summation over effective charges to compute polarization

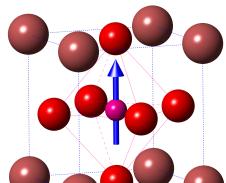


Zero-T energetic comparison of SnTiO_3 polymorphs

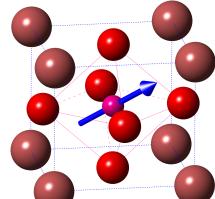
Perovskites:



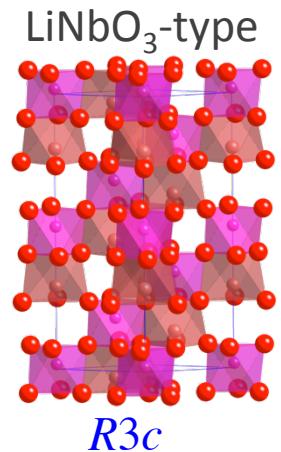
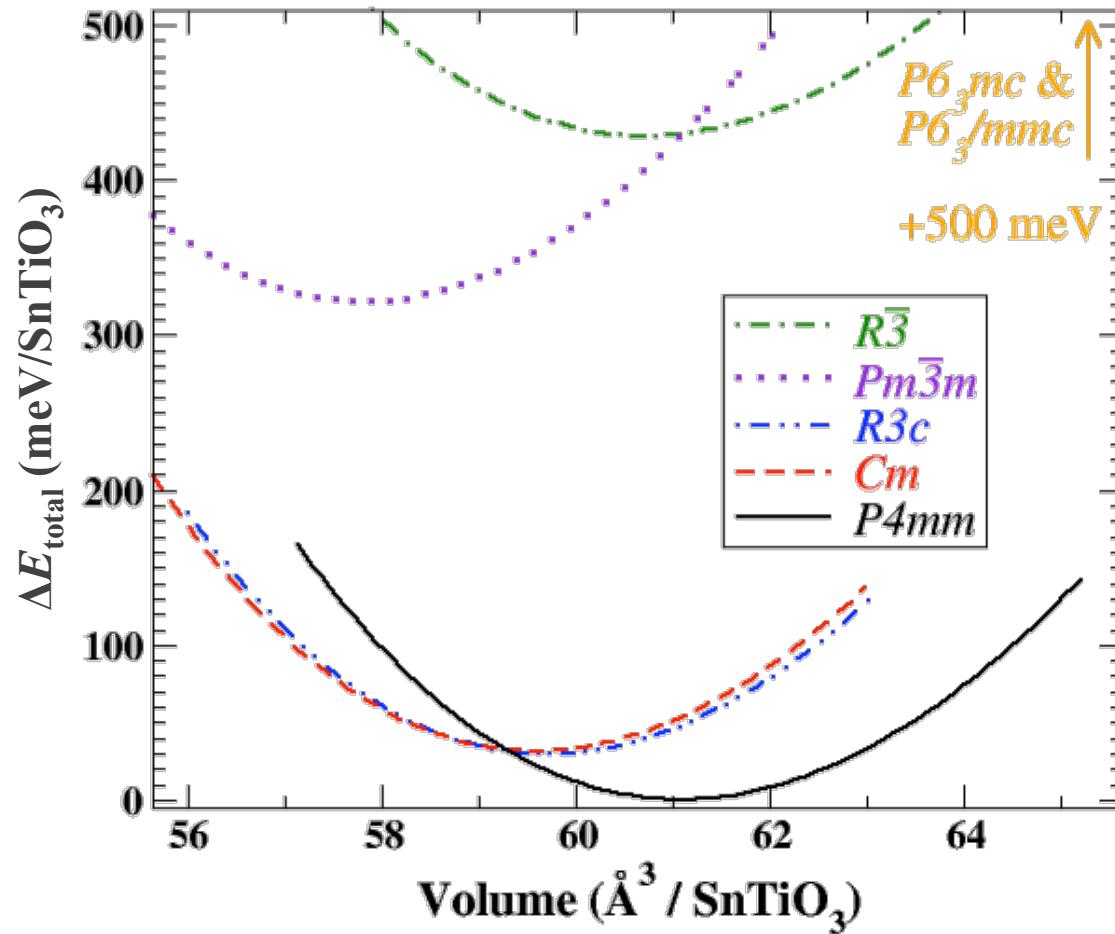
$Pm\bar{3}m$
(non-polar)



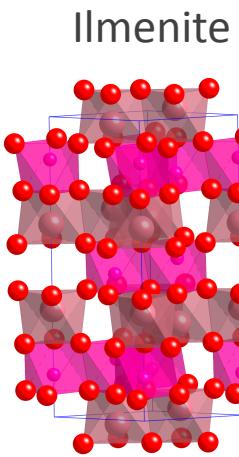
$P4mm$



Cm



$R3c$

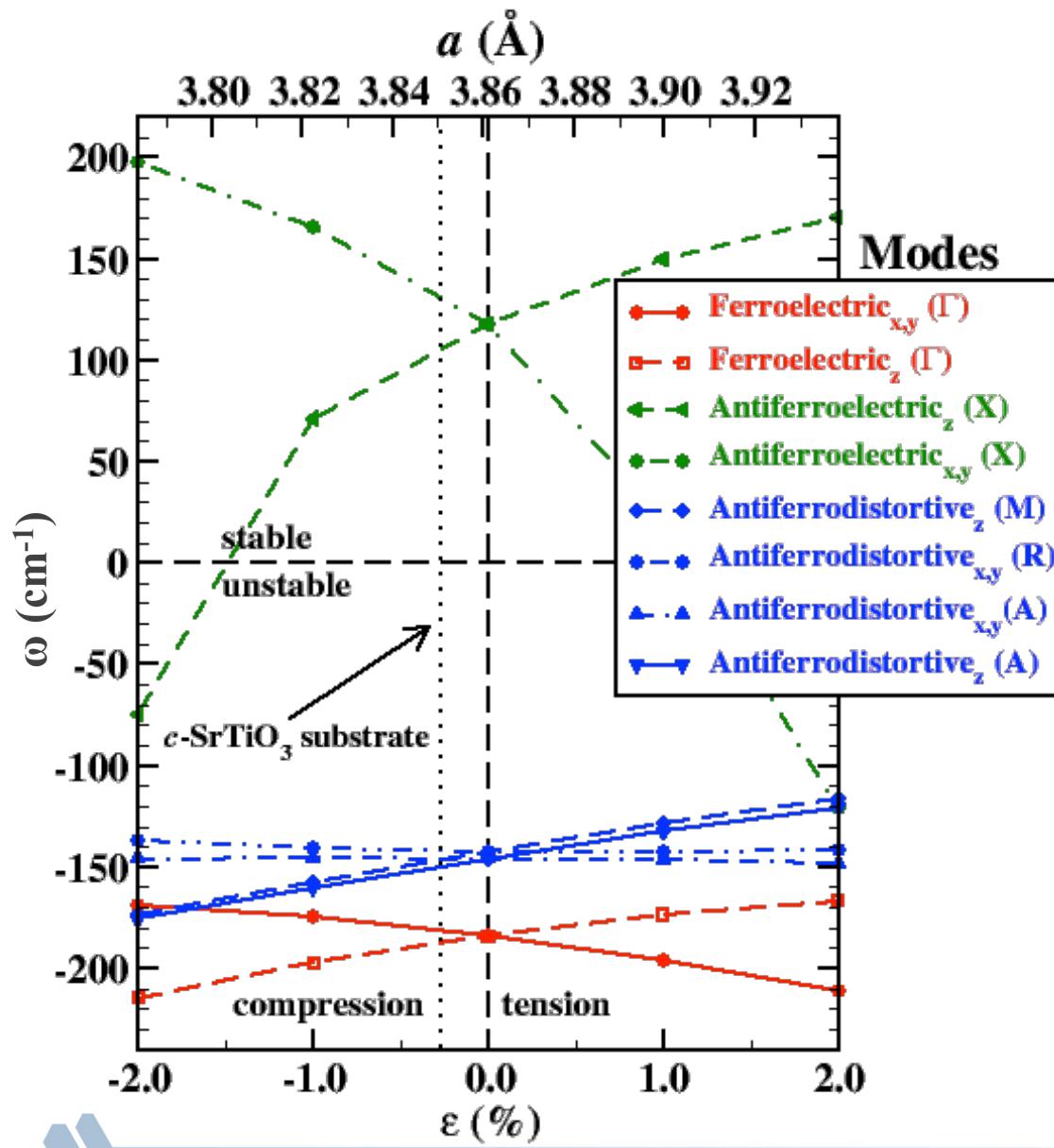


$R\bar{3}$
(non-polar)

- Perovskite $P4mm$ phase of SnTiO_3 lies lowest in energy
- Cm and $R3c$ polar phases have slightly higher energies.
- Can $R3c$ phase be stabilized by an appropriate choice of epitaxy?



Phonon instability analysis for perovskite SnTiO_3

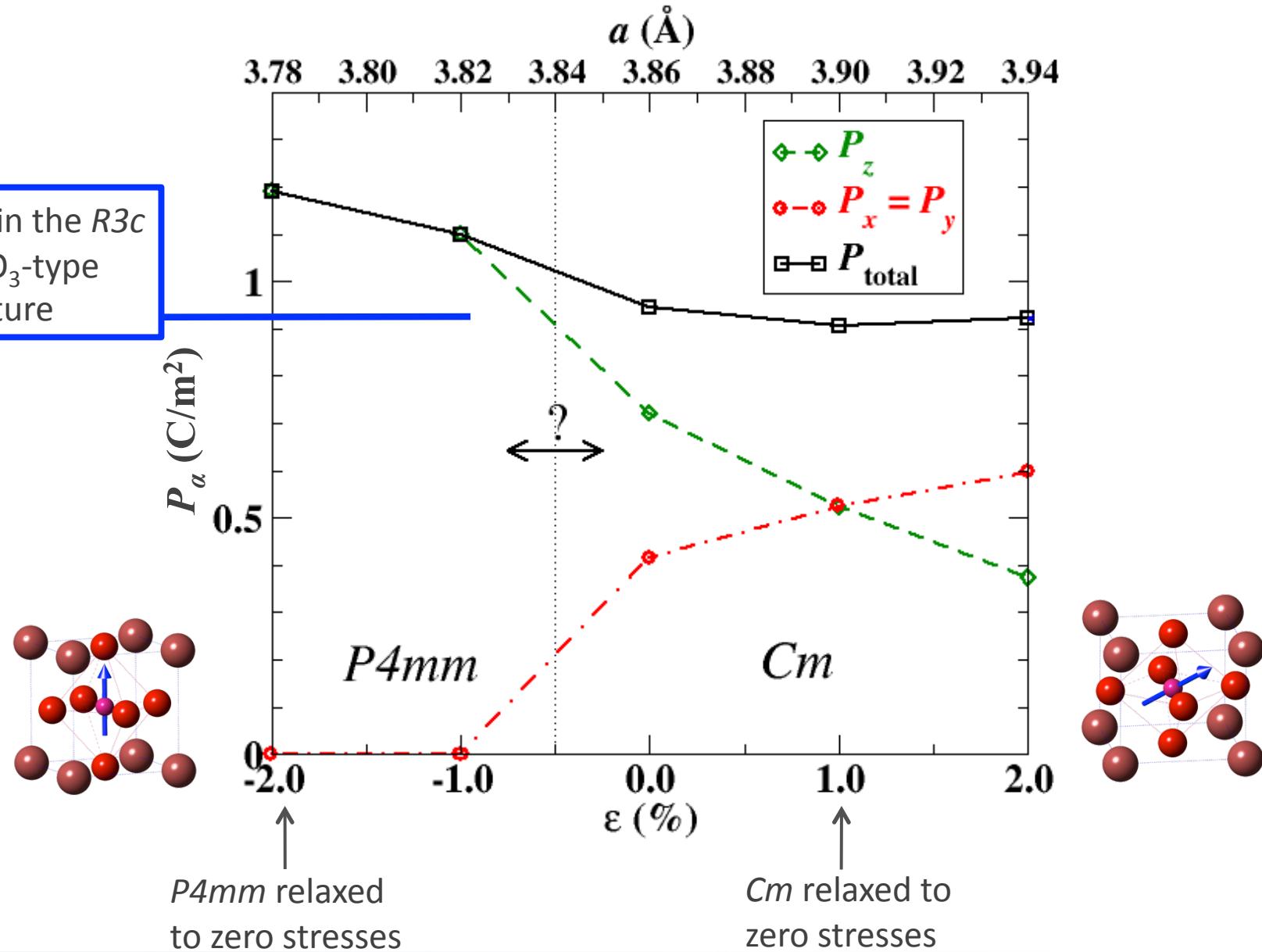


- Use relaxed cubic ($Pm\bar{3}m$) structure as a reference
- Tension stabilizes the Cm phase:
 $P_x = P_y \neq 0, P_z \neq 0$
- Compression stabilizes the $P4mm$ phase:
 $P_x = P_y = 0, P_z \neq 0$
- Antiferrodistortive rotations are not present in the stable epitaxial phases

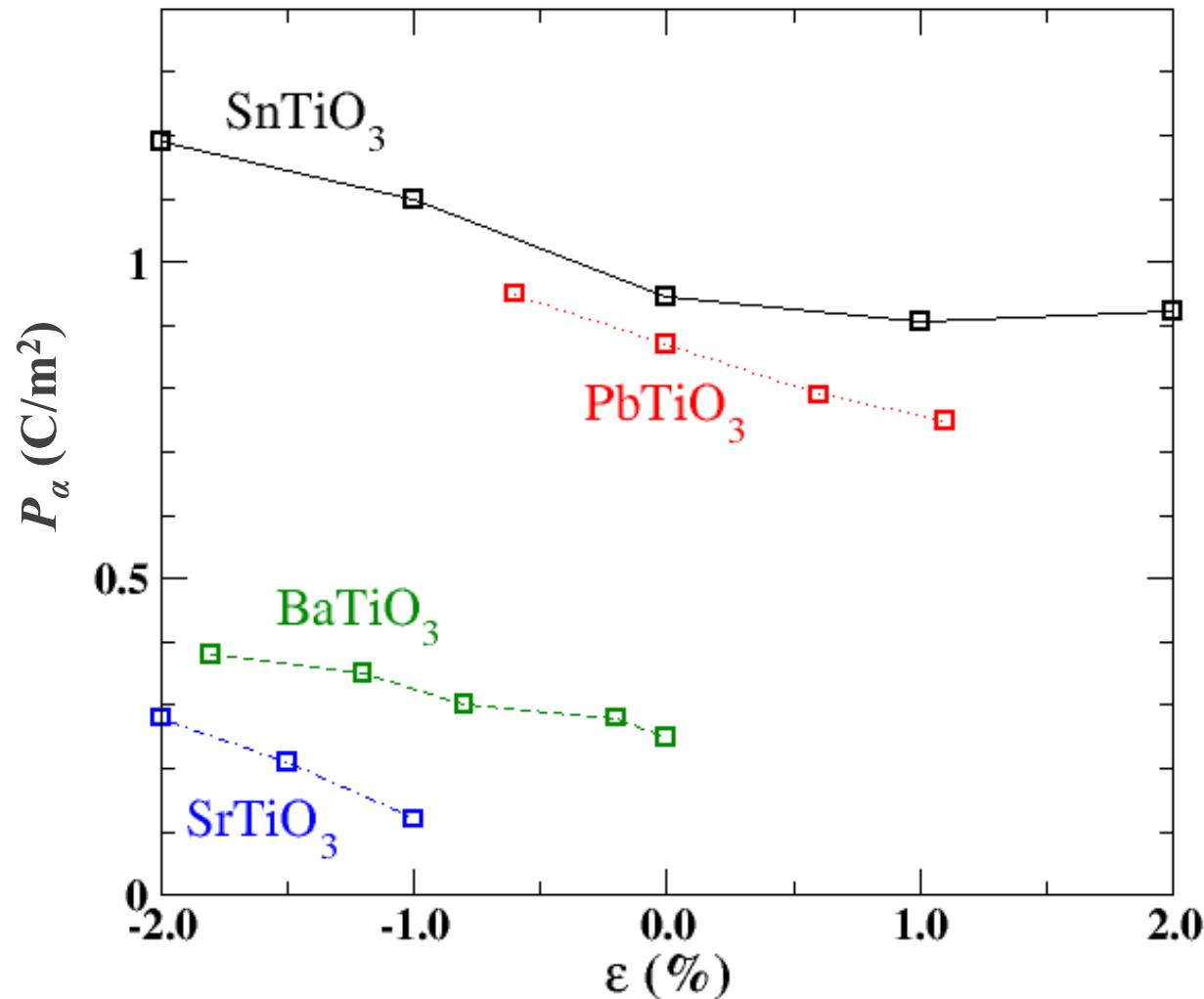


Polarization change with epitaxial strain in perovskite SnTiO_3

P_{total} in the $R3c$
 LiNbO_3 -type
structure



SnTiO_3 has large polarization compared to other perovskite ferroelectrics

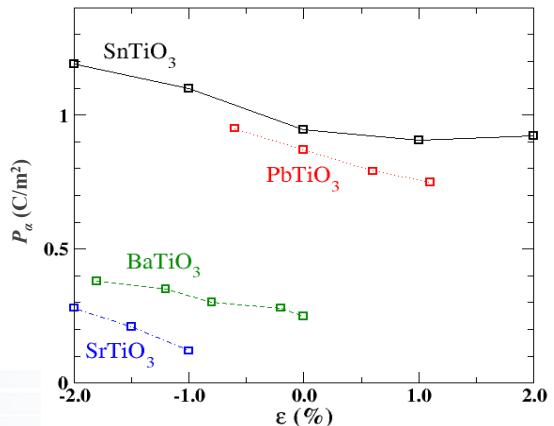
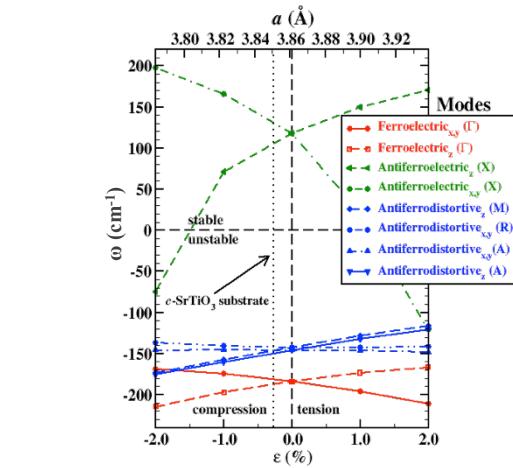
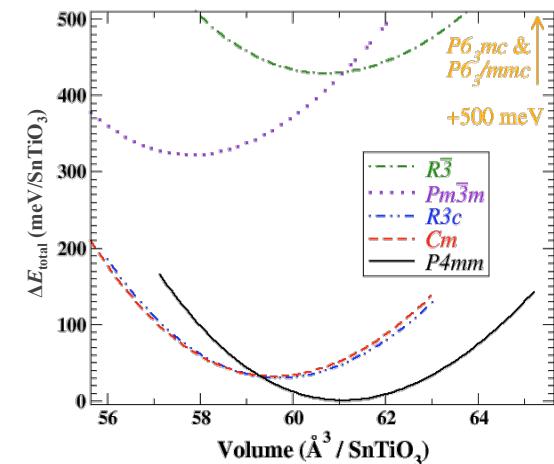


First-principles estimates of polarization in $P4mm$ titanates taken from Picozzi and Ederer, J. Phys.: Condens. Matter (2009) and Antons *et al.*, PRB (2005)



First principles analysis predicts stable ferroelectric perovskite SnTiO_3

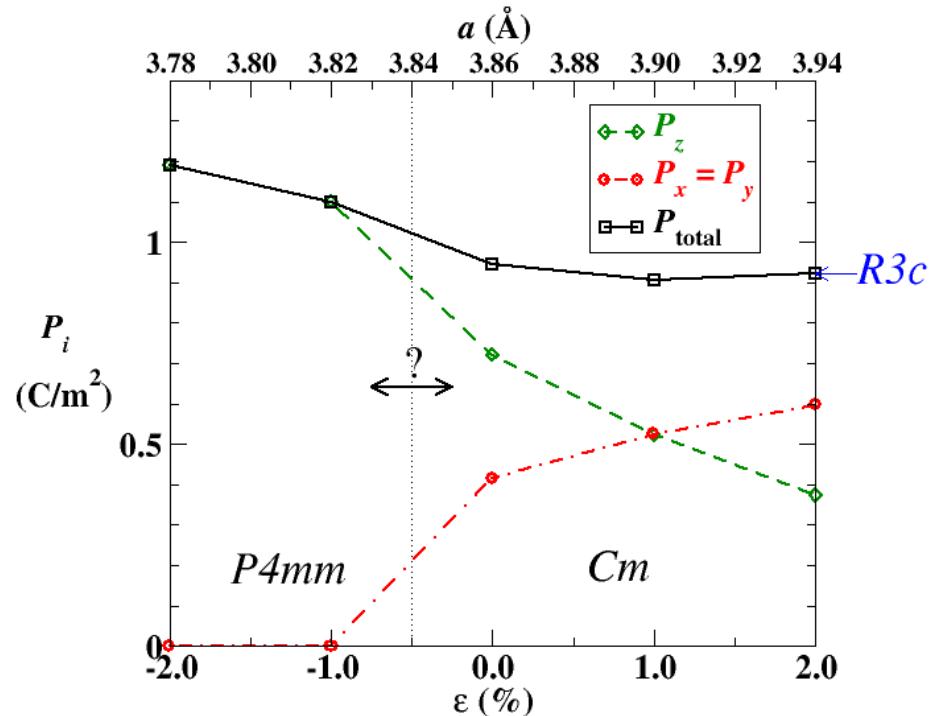
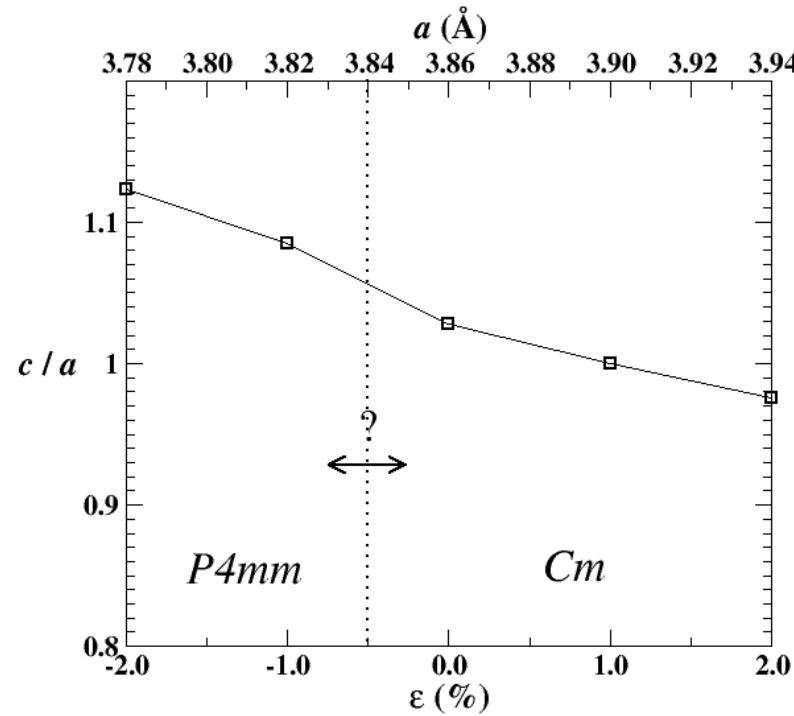
- $P4mm$ perovskite SnTiO_3 has lower energy than trigonal ($R3c$, $R\bar{3}$), hexagonal ($P6_3mc$, $P6_3/mmc$) and other tetragonal phases (Cm)
- Instability analysis predicts ferroelectric distortions of the high-symmetry structure both under tension and compression
- $P4mm$ perovskite SnTiO_3 has polarization of $\approx 1.2 \text{ C/m}^2$, larger than other perovskite titanates



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Tetragonality mostly follows polarization



GGA (PW91) orders SnTiO₃ phases similarly to LDA

	$E - E[P4mm]$ (eV)	
	LDA	GGA (PW91)
<i>R</i> 3 <i>c</i>	0.031	0.157
<i>Cm</i>	0.032	0.168
<i>R</i> -3	0.428	0.548
P6 ₃ mc	2.000	1.914

Structures relaxed in LDA,
GGA relaxation lowers *Cm*-*P4mm* difference to 0.095 eV



Berry-phase estimate of polarization yields comparable values to Born effective charge

	P_{total} (C/m ²)	
	<i>Born effective charge</i>	<i>Berry phase</i>
$P4mm$	1.191	1.274
$R3c$	0.922	1.077



R3c SnTiO₃ is comparable to other *R3c* oxides

DFT-calculated parameters for *R3c*-structure ternary oxides:

	<i>a</i> (Å)	<i>c</i> (Å)	A-ion z-displacement	<i>P</i> (C/m ²)	Ref.
SnTiO ₃	5.499	13.621	0.048	0.93	
ZnSnO ₃	5.262	14.003	0.036	0.50	[1]
LiNbO ₃	5.151	13.876	0.033	0.80	[2]
BiFeO ₃	5.460			0.84	[3]

1. Zhang *et al.*, Phys. Chem. Chem. Phys. (2010)
2. Veithen and Ghosez, PRB (2002)
3. Neaton *et al.*, PRB (2005)



Comparison with previous studies of SnTiO_3 —polar perovskite ($P4mm$) parameters

Core-electron treatment	a (Å)	c/a	P_z (C/m ²)	Ref.
Pseudopotential (NC?)	3.80	1.08	0.73	[1]
All-electron (FLAPW)	3.812	1.115	1.28	[2]
Pseudopotential (US)	3.799	1.09	1.1	[3]
Pseudopotential (US)	3.784	1.134	1.191	This work

1. Konishi *et al.*, MRS Symp. Proc. (2003)
2. Uratani *et al.*, Jpn. J. Appl. Phys. (2008)
3. Matar *et al.*, Chem. Phys. (2009)



Comparison with previous studies of SnTiO₃—perovskite(*P4mm*)-ilmenite(*R3c*) energy difference

Core-electron treatment	Exchange-correlation potential	$E[P4mm] - E[R-3]$	Ref.
Pseudopotential (PAW)	GGA (PBE)	-0.130	[1]
Pseudopotential (US)	LDA	0.428	This work
Pseudopotential (US)	GGA (PW91)	0.548	This work
Pseudopotential (PAW)	GGA (PBE)	0.398	This work

Structures for this work relaxed in LDA,
GGA relaxation lowers *Cm-P4mm* difference from 0.168 eV to 0.095 eV

1. Hautier *et al.*, Chem. Mat. (2010)



All-electron results support pseudopotential use

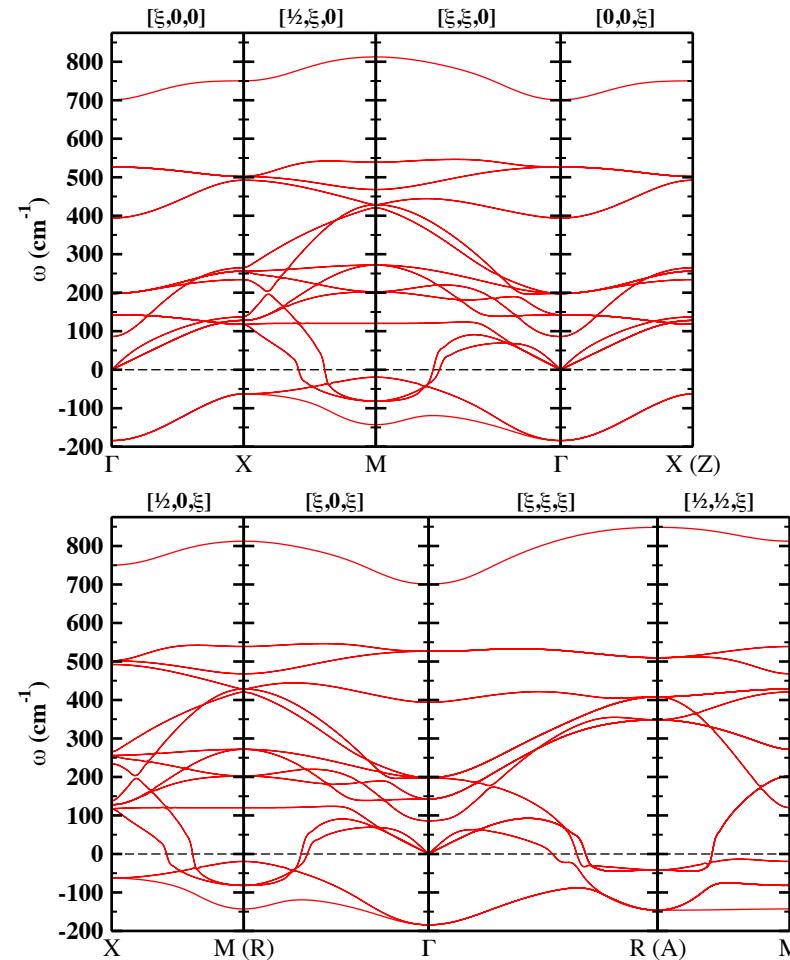
Cubic ($Pm\overline{3}m$) SnTiO_3

	a (Å)	B (GPa)	E_{gap} (eV)
All-electron (FLAPW)	3.873	205	1.1
Pseudopotential (ultrasoft)	3.867	206	1.1

- a and B from Birch-Murnaghan equation of state fit to 7 unrelaxed volumes at varying a
- E_{gap} estimated from density of states



Phonon dispersion plot for $Pm\bar{3}m$ SnTiO_3 shows instabilities throughout the Brillouin zone



Polar perovskite ($P4mm$) SnTiO_3 has only stable phonon modes

